

# Design of High Performance, High Energy Cathode Materials

Marca M. Doeff-Principal Investigator  
Energy Storage and Distributed Resources Division  
Lawrence Berkeley National Laboratory

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

## Timeline

- **Project start date 10/1/2011**
- **Project end date 9/30/2015**
- **Percent complete 94%**

## Budget

- Total project funding
  - DOE (\$1900k)
  - Contractor share
- Funding received in FY14 \$400k
- Funding for FY15 \$500k

## Barriers

- **Barriers addressed**
  - ↳ Energy Density
  - ↳ Cost
  - ↳ Cycle Life

## Partners

- Interactions/ collaborations
  - LBNL, BNL, SSRL, UCB, UCSD, NREL
- Project lead LBNL

## ● Objectives

- Synthesize high energy, high performance cathode materials with an emphasis on modified stoichiometric NMCs, using spray pyrolysis and other methods
- Understand effect of high voltage cycling on NMCs
- Understand effect of Ti-substitution on NMCs

## ● Relevance

- Improving NMCs to increase capacity by cycling to higher voltages is the fastest route to the higher energy density batteries needed for vehicle applications
  - ✦ Ti-substituted NMCs show improved practical capacity (up to 225 mAh/g) and better high voltage cycling than baseline materials
  - ✦ Ti-substituted NMCs are structurally stable and do not exhibit voltage fade like layered-layered composites
- Spray pyrolysis is an attractive, one-step method for preparation of spherical particles (good for processing). Coated and composite materials can be made in either one or two steps
- Higher energy, simpler processing= lower costs per kWh

# Milestones-FY 14 and FY15

date	Milestone and go/no-go decisions	Status
Dec. '13	Complete optimization of Ti-NMC synthesis with $\text{TiOSO}_4$	Discontinued and effort transferred to ABR project
Mar. '14	Go/no-go decision on infiltration of $\text{LiFePO}_4$ into $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$	No-go. Decision made to concentrate on NMCs
Jun. '14	Complete soft XAS experiments on Ti-NMCs	Completed. Papers published in Nat. Comm., E&ES, and JMCA
Sept. '14	Go/no-go decision on spray pyrolysis of NMCs	Go decision, based on superior performance of spray pyrolyzed NMCs. Paper in preparation
Dec. '14	Complete synchrotron x-ray Raman experiments on representative NMCs	Completed on schedule. Paper in preparation.
Mar. '15	Finish survey of composites made with spray pyrolyzed NMC hollow particles	Postponed due to equipment issues.
Jun. '15	Demonstrate feasibility of coating NMCs with ALD or spray pyrolysis techniques to improve high voltage performance (go/no go)	ALD experiments underway with Chunmei Ban (NREL)
Sept. '15	Select best-performing materials	On track.

- **Use synchrotron techniques to understand effects of high voltage cycling on NMCs**
  - ↳ -goal is to increase capacity without sacrificing performance
- **Understand effect of Ti substitution in NMCs**
- **Synthesize NMCs by spray pyrolysis techniques and compare to conventionally made materials**
  - ↳ Understand what leads to differences in behaviors
  - ↳ Make composites by filling hollow particles made by spray pyrolysis
  - ↳ Coat using spray pyrolysis techniques or ALD/MLD coatings (with Chunmei Ban)



# Previous Achievements

## Objective

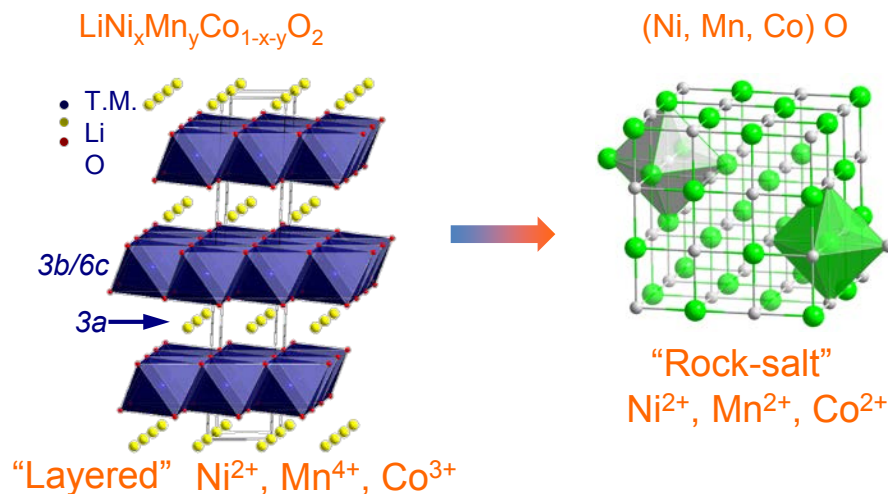
Understand the fundamental mechanism that governs the electrode behaviors under high-voltage cycling conditions. Use as a guide to develop new synthetic and/or processing techniques for high performance, high energy density cathode materials.

## Identified Challenges

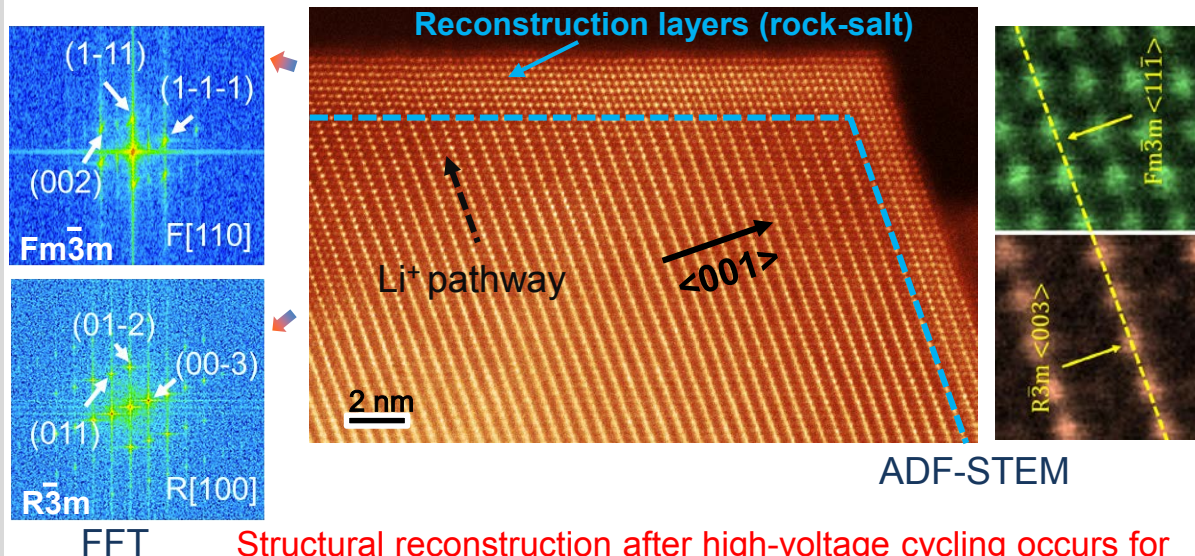
- Electrode-electrolyte reactivity;
- Surface reconstruction from the layered structure to a rock-salt/spinel mixed structure;
- Irreversible reduction of transition metals (i.e., Mn, Co) at the surface of cathode particles;
- The surface reconstruction tends to build up as the cycle number increases and is greater for cycling to high voltages.

## Previous Conclusion (FY 14)

Structural reconstruction (R-3m to Fm-3m transition) and chemical evolution (formation of a surface reaction layer) at the surface of  $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$  particles. These are associated with capacity fading and impedance buildup during high-voltage cycling.



Lin, Markus, Nordlund, Weng, Asta, Xin & Doeff. Nat. Commun. 5, 3529 (2014)



Structural reconstruction after high-voltage cycling occurs for both NMCs and Ti-containing NMCs

# Technical Accomplishments/Progress

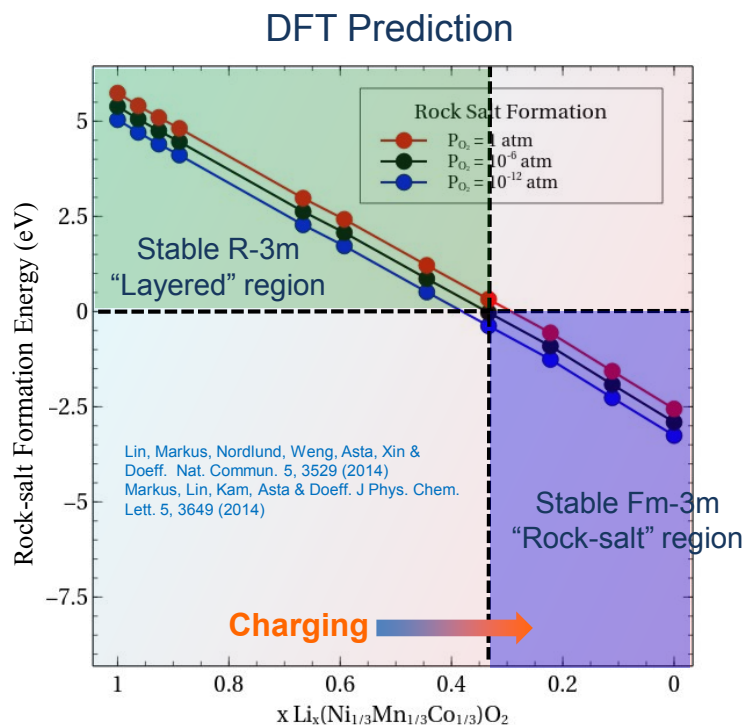
## Scientific Question

When does the surface reconstruction layer build up during the electrochemical cycling? When is it first created when being cycled from the pristine state?

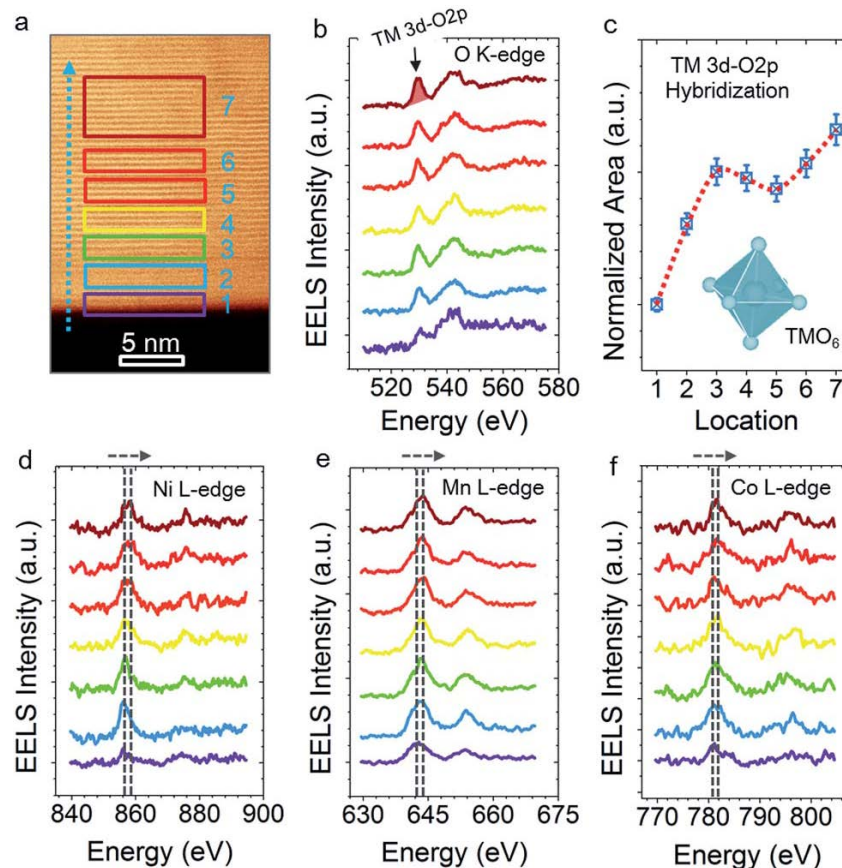
## Approach

DFT theoretical calculations to identify the driving force for the structural transition

Experimentally verify the calculation using electron energy loss spectroscopy for the cathode particles that are at different states of charge (voltage vs.  $\text{Li}^+/\text{Li}$ )



## EELS study of particles in the charged state (4.7 V vs. $\text{Li}^+/\text{Li}$ )



Lin, Nordlund, Markus, Weng, Xin & Doeff. Energy Environ. Sci. 7, 3077 (2014)

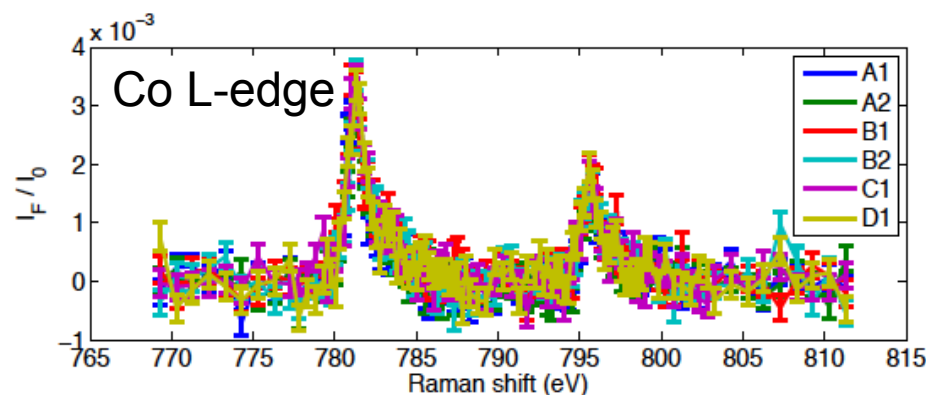
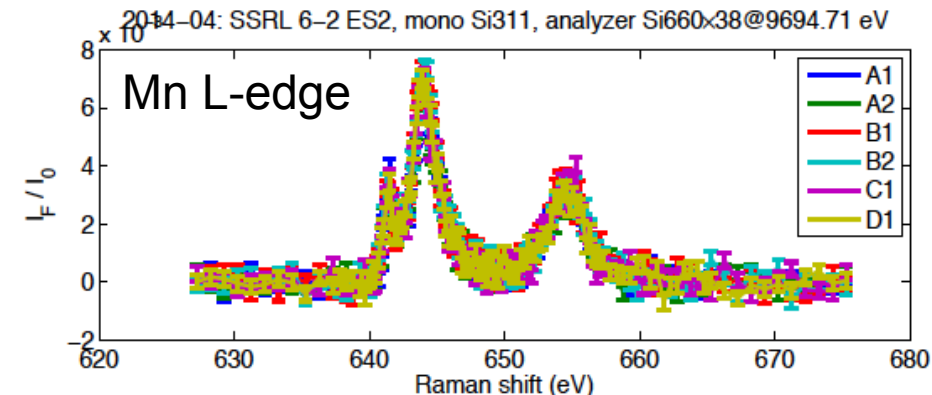
## Conclusion

This result shows that the oxidation states of transition metals are lower on surfaces than in the bulk for the particles after the first charge to 4.7 V vs.  $\text{Li}^+/\text{Li}$ ; surface reconstruction has occurred in the very first cycle.

Continued from the last slide

Particle surfaces are sensitive to lithium removal, how about the bulk? In order to study the bulk effect, we performed transition metal L-edge X-ray Raman spectroscopy (“bulk version of soft X-ray absorption spectroscopy”) using the state of the art beam line 6-2 at SSRL, in collaboration with Tsu-Chien Weng, Dimosthenis Sokaras and Dennis Nordlund.

Co-ppt NMC-442



SOC A1 < A2 < B1 < B2 < C1 < D1 (chemical delithiation)  
 pristine  $\longrightarrow$  x=0.4

It is clear from the XRS results that there are no obvious changes in the electronic structures of the bulk.



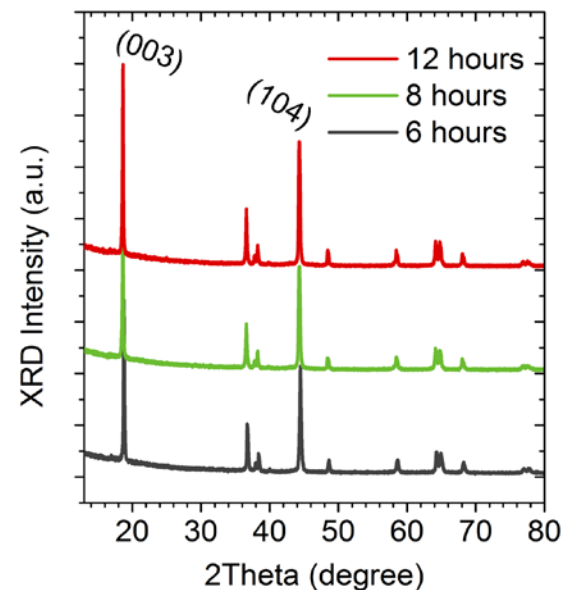
# Technical Accomplishments/Progress

## Scientific Question

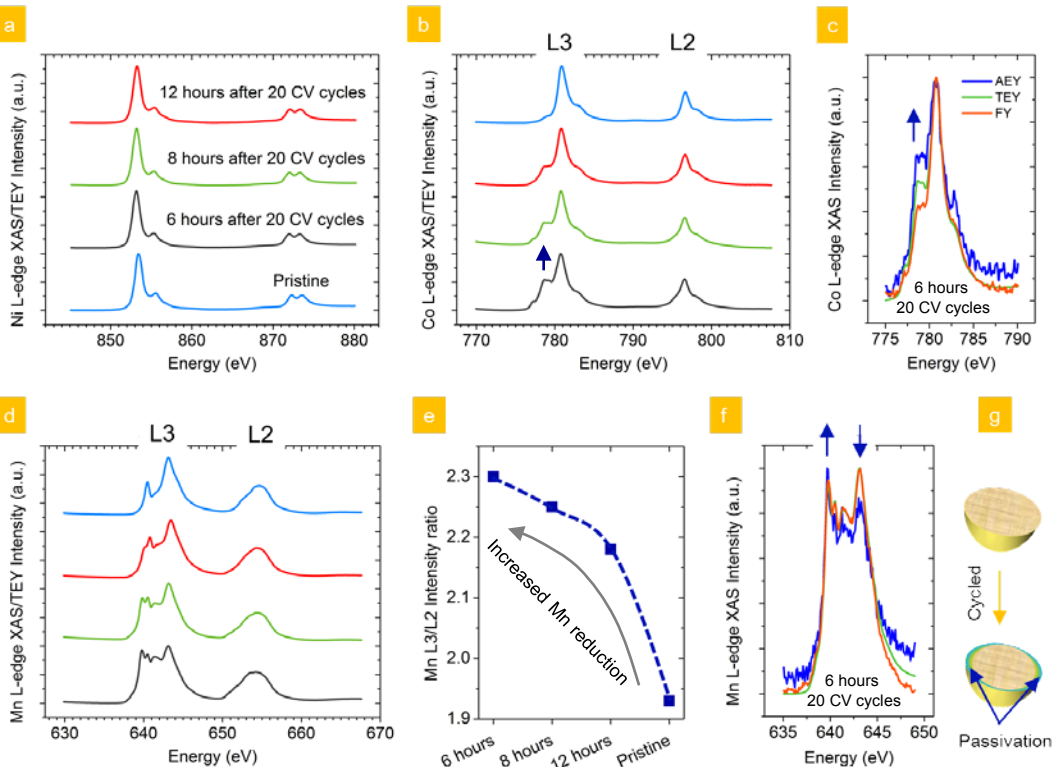
How do the materials synthesis conditions alter the behavior of surface reconstruction? Can we optimize the materials processing conditions to minimize the surface reconstruction phenomenon?

## Approach

The NMC materials were synthesized using conventional co-precipitation methods and annealed at an identical temperature (900 °C) for different periods of time (6 hours, 8 hours, and 12 hours). Electrodes were cycled in lithium half-cells for 20 CV cycles between 2.0-4.7 V vs. Li<sup>+</sup>/Li. The soft X-ray absorption spectroscopy was used to study oxidation states of transition metals on particle surfaces.



Powder X-ray diffraction (XRD) confirmed that the NMC materials have the expected R-3m layered structure, and these materials show very minor differences in the crystallinity.



## Conclusion

In general, longer annealing durations for the NMC442-2% Ti materials resulted in thinner surface passivation layers, higher coulombic efficiencies and better capacity retention during high voltage cycling in lithium cells.

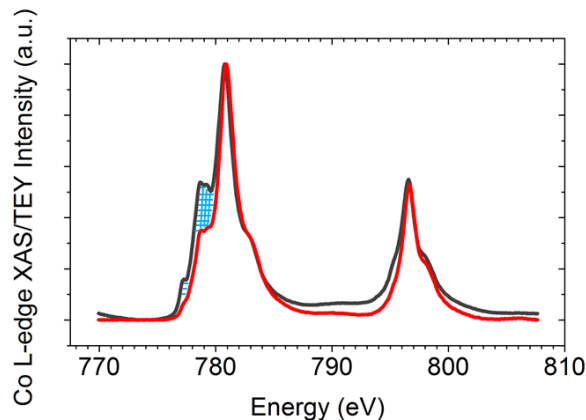
## Scientific Question

How do different cycling conditions affect surface reconstruction?

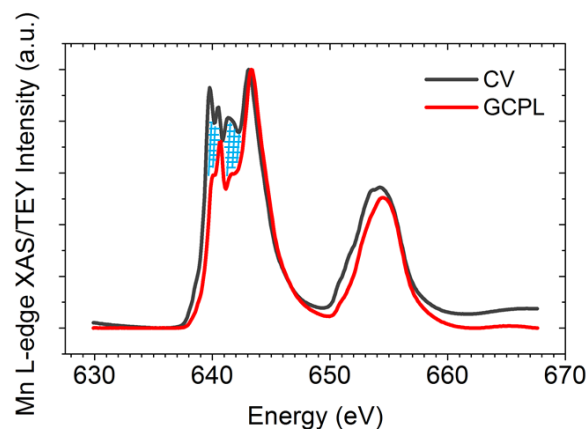
## Approach

Two identical electrodes containing NMC materials were prepared and electrochemically cycled in lithium half-cells using cyclic voltammetry and galvanostatic cycling for an identical number of cycles (20 charge-discharge cycles). The NMC materials were then analyzed by soft X-ray absorption spectroscopy.

a



b



Comparison of (a) Co L-edge and (b) Mn L-edge in NMC442-2%Ti (annealed for 6 hours) electrodes cycled for 20 cycles using CV (gray) or constant current conditions (red). The major spectral differences are marked with cross-hatching in (a) and (b). The measurements were performed using TEY mode. The current density for the constant current cycling was approximately 0.11 mA/cm<sup>2</sup> (21.4 mA/g). The first cycle discharge capacity and coulombic inefficiency were 192 mAh/g and 16.8%, respectively.

TEY probes ~5 nm into the surface

## Conclusion

The development of the surface reconstruction layer on the NMC materials was also influenced by the electrochemical technique used to cycle cells with cyclic voltammetry resulting in formation of more reduced transition metal on particle surfaces than the galvanostatic cycling, even though the exposure time to the electrolyte was drastically shorter in the former. These results illustrate the complex effects and interplay of synthesis and electrochemical history upon performance of NMC materials.

F. Lin, D. Nordlund, T. Pan, I. Markus, T.-C. Weng, H. Xin, and Marca M. Doeff, *J. Mater. Chem. A* **2**, 19833 (2014).

# Previous Achievements

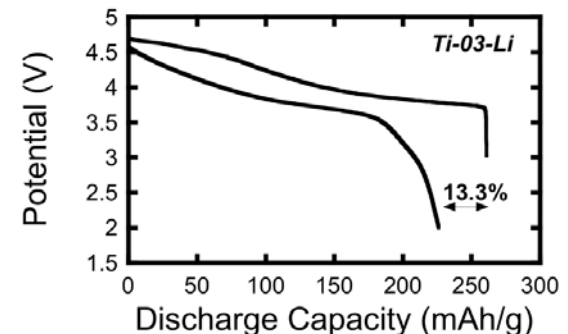
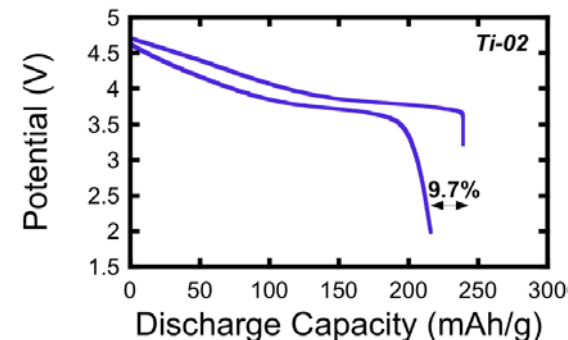
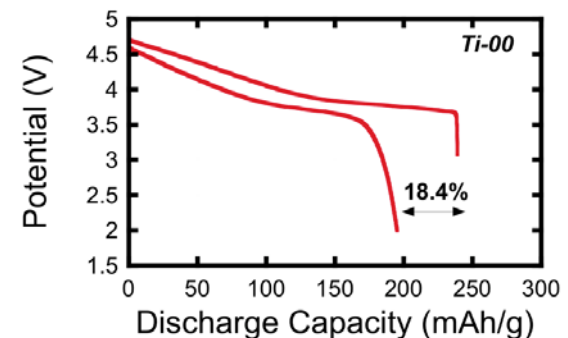
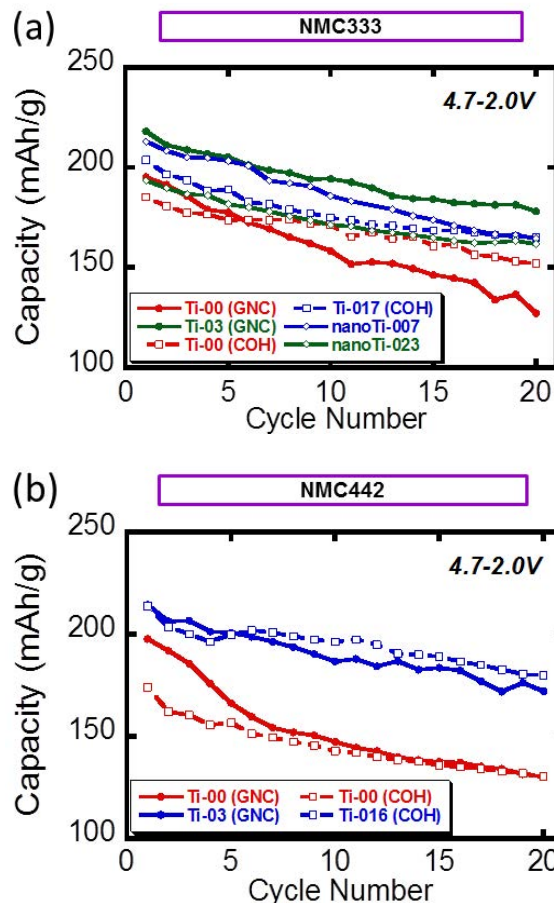
## Scientific Question

Previously we demonstrated that 2-4% Ti substitution on the Co site in regular NMC materials can improve the high voltage stability as well as increase specific discharge capacity. What are the fundamental reasons for this observation?

## Previous observations

- Partial Ti-substitution for Co in NMCs increases practical capacity
- Improvement is due to better first cycle efficiencies
- Both Li-excess and Li-stoichiometric compounds can be prepared
- Higher capacity and better cycling for Ti-substituted NMC442
- No difference between COH and GNC made samples for Ti-substituted NMC-442, indicating that the Ti-substitution method can be universal.

## Lithium half-cell cycling



Kinson Kam and Marca M. Doeff, *J. Mater. Chem.*, **21**, 9991 (2011).

Kinson C. Kam, Apurva Mehta, John T. Heron, and Marca M. Doeff, *J. Electrochem. Soc.*, **159**, A1383 (2012).

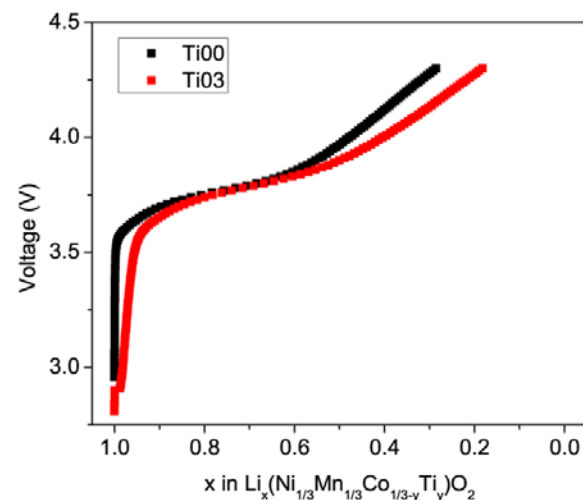
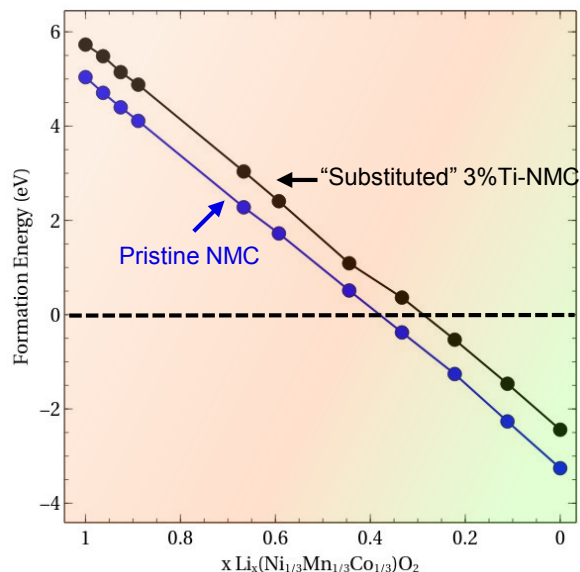
# Technical Accomplishments/Progress

## Scientific Question

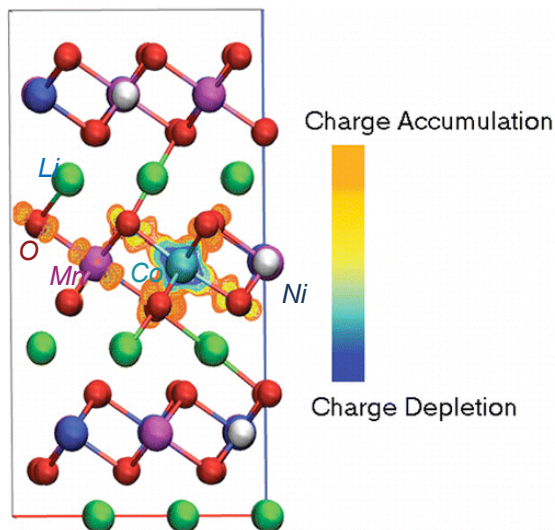
Previously we demonstrated that 2-4% Ti substitution on the Co site in regular NMC materials can improve high voltage cycling as well as increase specific discharge capacity. What are the fundamental reasons for this observation?

## Approach

DFT calculations were performed to reveal the theoretical mechanism, and verified with experiments.



Voltage profiles from slow stepped potential experiments



## Conclusion

Ti substitution **reduces the structural distortions** occurring during delithiation due to the larger cation radius of  $\text{Ti}^{4+}$  relative to  $\text{Co}^{3+}$  and the presence of **an electron polaron on Mn cations** induced by aliovalent Ti substitution. The structural differences were found to correlate with **a decrease in the lithium intercalation voltage at lower lithium concentrations**, which is consistent with quasi-equilibrium voltages obtained by integrating data from stepped potential experiments. Furthermore, **Ti is found to suppress the formation of a secondary rock salt phase at high voltage.**



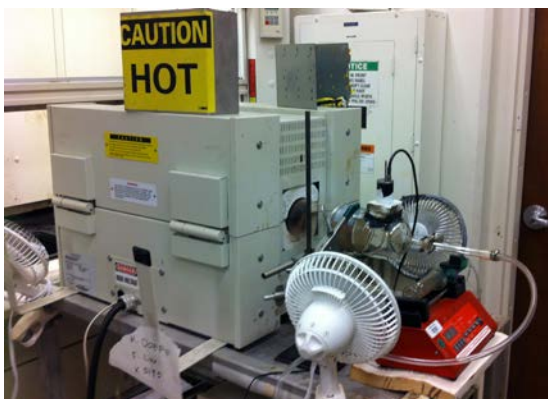
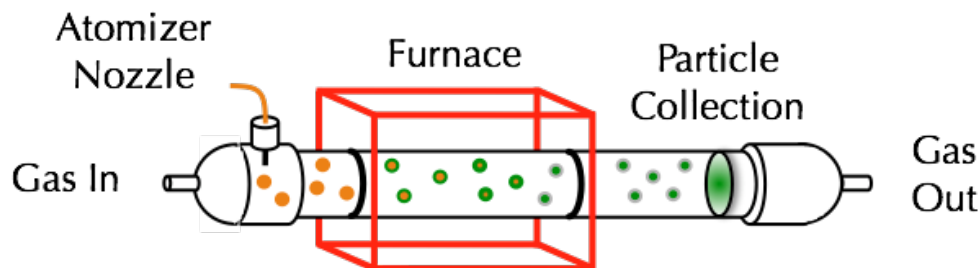
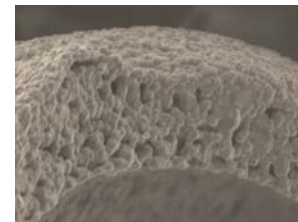
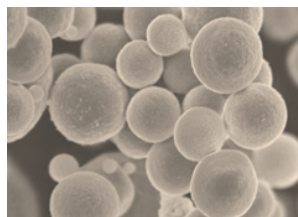
## Scientific Question

Other than the Ti-substitution, can we develop other synthetic techniques to inhibit the surface reconstruction?

## Approach

- Spray pyrolysis
- Atomic layer deposition.

Spray pyrolysis to generate fused agglomerations



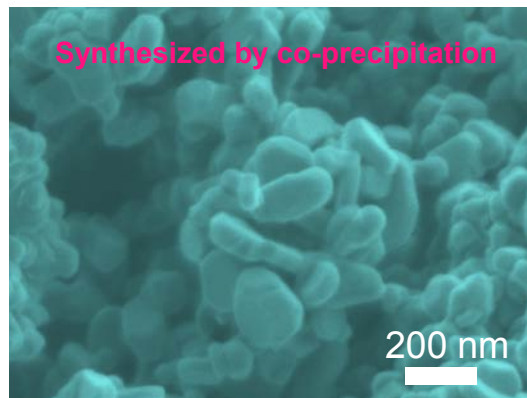
# Technical Accomplishments/Progress

## Scientific Question

Other than the Ti-substitution, can we develop other synthetic techniques to inhibit the surface reconstruction?

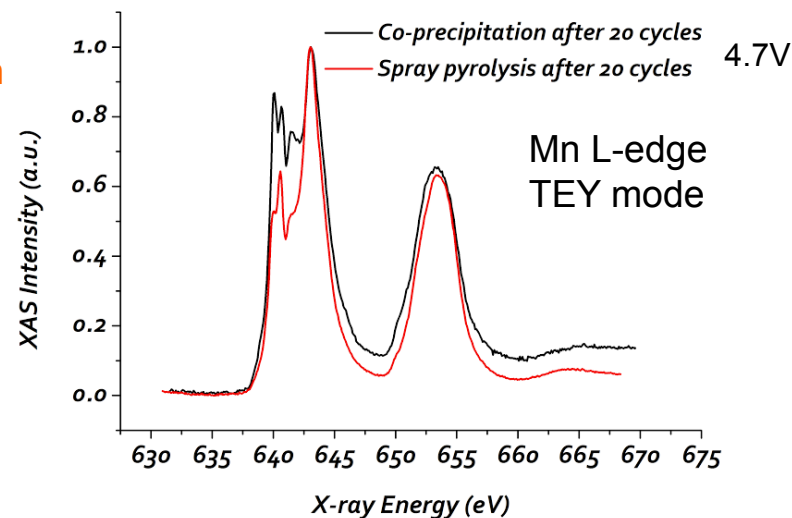
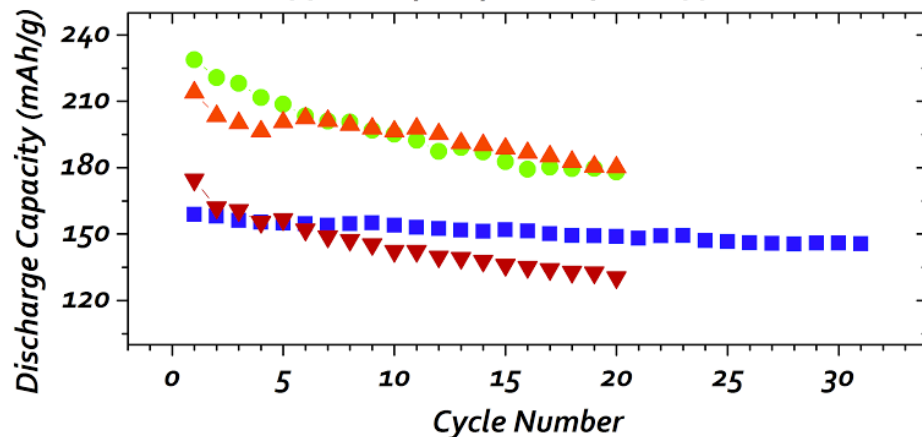
## Approach

- Spray pyrolysis
- Atomic layer deposition.



## Much improved high voltage cycling performance with spray pyrolysis

- 2.0-4.3 V (Spray Pyrolysis, NMC<sub>442</sub>)
- 2.0-4.7 V (Spray Pyrolysis, NMC<sub>442</sub>)
- ▲— 2.0-4.7 V (Co-precipitation, ~2% Ti-NMC<sub>442</sub>)
- ▼— 2.0-4.7 V (Co-precipitation, NMC<sub>442</sub>)



After 20 cycles using identical electrochemical protocol, significantly less surface reconstruction was observed in the NMC materials prepared by spray pyrolysis, which explains the improved cycling performance

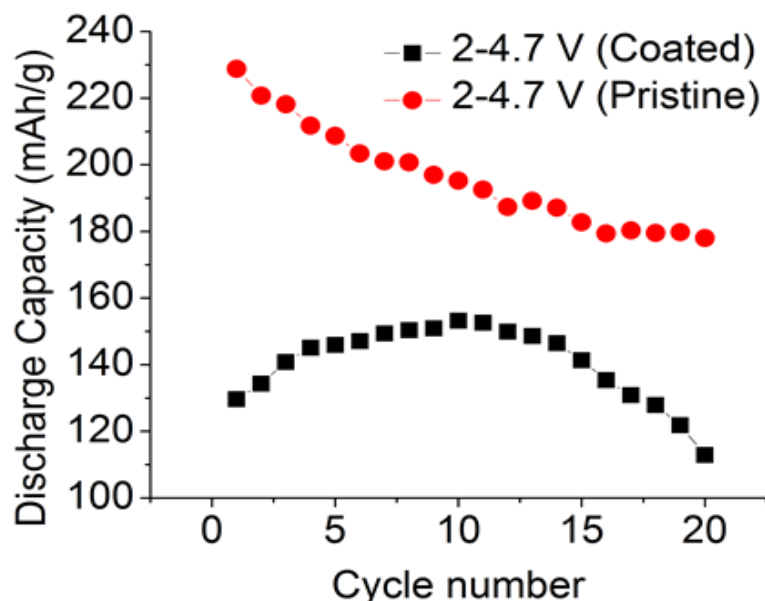
## Scientific Question

Other than the Ti-substitution, can we develop other synthetic techniques to inhibit the surface reconstruction?

## Approach

- Spray pyrolysis
- Atomic layer deposition.

Early steps of atomic layer deposition has been initiated and more experiments are being planned in collaboration with Chunmei Ban of NREL



ALD coating was also applied to spray pyrolysis produced NMC materials. The preliminary results showed that the 1 nm  $\text{Al}_2\text{O}_3$  coating on the electrode surface did impact cycling performance. The coating behaves like a passivation layer and reduces the practical capacity. The electrode underwent an activation period and then slowly degraded (black curve in Figure 1e). More efforts on the coating protection are being implemented, and the improvement on the cycling stability is still possible.

# Response to Reviewers' Comments

- **Ti-NMCs still exhibit significant capacity fading during cycling to high potentials.**

↪ *While some Ti-NMCs appear to cycle better than baseline materials to 4.7V, capacity fading is still significant. Our work was designed to understand the origins of the losses in both types of materials. Computational work (in collaboration with the Asta group at UCB) indicates that Ti-substitution does have a beneficial effect, but more will need to be done to improve high voltage cycling, including using specially designed electrolytes, employing coatings, etc.*

- **Spray pyrolysis results in hollow particles, which leads to poor tap density**

↪ *Increasing residence time solves the problem of hollow particles, but requires additional equipment, which we don't have right now. Instead, we are investigating the possibility of infiltrating particles with a second phase to form core-shell materials.*

- **The PI is a careful worker and a fountain of knowledge about research at LBNL.**

↪ *I appreciate the compliments.*



# Collaborations and Coordination

- **This is a single investigator project funded under BATT and BMR.**
  - ➡ No formal collaborations are funded through this work
  - ➡ BUT, we informally collaborate with scientists both inside and outside LBNL and publish papers.

Collaborator	Institution	Nature of Collaboration
Prof. M. Asta	UC Berkeley	Computation on Ti-NMCs. Shared graduate student (Isaac Markus)
A. Mehta, D. Nordlund, T.-C. Weng, D. Sokaras, Y. Liu	SSRL	Synchrotron XRD, Raman, imaging, and XAS experiments
Huolin Xin	BNL	STEM-EELS, high resolution TEM
Haimei Zheng	LBNL	In situ TEM (planned)
Prof. T. Rojo	CICEnergigune, Spain	Cathode studies (hosted a graduate student, Amaia Iturrondobeitia)
G. Chen, R. Kostecki, K. Persson, M. Salmeron	LBNL	Cathodes and solid electrolytes
E. Crumlin, N. Tamura	ALS/LBNL	Synchrotron studies on solid electrolytes
C. Ban	NREL	ALD and MLD coatings
S. Meng	UCSD	cathodes

# Remaining Challenges and Barriers

- **High voltage cycling of NMCs presents many challenges**
  - ↪ Stability of electrode materials
  - ↪ Electrode/electrolyte interfaces
  - ↪ We've been looking at cycling to 4.7V vs.  $\text{Li}^+/\text{Li}$ -very high voltages!
  - ↪ Can we back off on the high potentials a bit (4.5V, 4.4.V...) and increase capacities another way (e.g., increase Ni content)?
  - ↪ Dahn's additives have shown some promise for high voltage cycling
- **No single strategy is 100% effective for high voltage cycling**
  - ↪ We will need to use combinations of strategies
  - ↪ Additives and special electrolytes
  - ↪ Substitutions
  - ↪ Coatings
- **Synthesis conditions and electrochemical history affect results in subtle ways**
  - ↪ Surface chemistries of pristine materials may be critical
  - ↪ Need a better understanding of this

- **This project ends in October 2015**

- ↳ Composite core-shell structures made by spray pyrolysis
- ↳ Coated materials

- **A new project, if funded, will be a multi-investigator effort at LBNL geared towards increasing the capacities of cathode materials through multiple synthetic and diagnostic thrusts.**

- ↳ Will include NMCs but not be limited to them
- ↳ Will work on higher Ni content NMC compositions to increase capacity further
- ↳ Preparation of core-shell materials using spray pyrolyzed hollow spheres will be carried over, if initial results warrant.

# Summary

- Surface reconstruction of NMCs to rock salt/spinel occurs during cycling and is more severe for high voltage cycling than normal cycling.
- Aliovalent Ti-substitution in NMCs lowers the potential profile, allowing extraction of more lithium between set voltage limits. It also delays onset of surface rock salt formation, but does not prevent it entirely.
- Degree of transition metal reduction (surface reconstruction, etc.) on particle surfaces during cycling depends on synthesis conditions and electrochemical history.
- Spray pyrolyzed samples appear to perform better than co-precipitated samples. Improvement is similar to effect of Ti-substitution.
- Results suggest that the surface chemistries of pristine samples may be important. Further study of this is needed.